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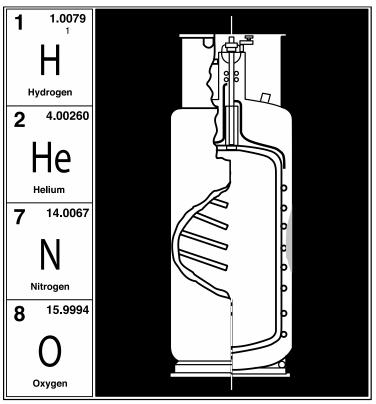
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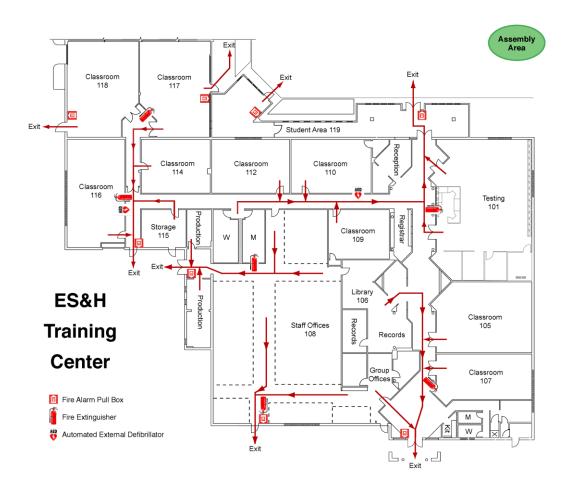
# Cryogen Safety COURSE 8876



May 2017



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# Introduction

#### **Course Overview**

Cryogenics (from the Greek word κρυος, meaning *frost* or *icy cold*) is the study of the behavior of matter at very cold temperatures. The purpose of this course is to provide trainees with an introduction to cryogen use, the hazards and potential accidents related to cryogen systems, cryogen safety components, and the requirements that govern the design and use of cryogen systems at Los Alamos National Laboratory (LANL). The knowledge you gain will help you keep your workplace safe for yourself and your coworkers.

# **Course Objectives**

When you complete this course, you will be able to recognize

- definitions associated with cryogens, along with properties, examples, and uses of cryogens;
- hazards and controls associated with cryogen use;
- organizations, documents, and standards that affect cryogen use;
- roles and responsibilities of individuals and groups in maintaining safe cryogen operations at LANL; and
- whom to contact for more information, for workplace evaluations, or in case of emergency.

# **Program Owner**

This course was developed under the direction and technical oversight of Occupational Safety and Health Division (OSH-DO), the functional program owner for this training.

# **Target Audience**

This course is designed for cryogen users at LANL.

#### **Course Limitations**

This course does not address every type of hazard and control that may be associated with cryogen systems, nor does it address sitespecific cryogen hazards and controls. This course does not eliminate the need for site-specific training. This course does not address every requirement for the use of cryogens specified in LANL Procedure (P) P101-5, Cryogens.

#### **About This Course**

This course consists of an introduction, three learning modules, and a resources and references section. The class duration is 2½ hours.

# **Acronyms**

AET-1 Mechanical and Thermal Engineering (Group)
ASME American Society of Mechanical Engineers
BLEVE boiling-liquid expanding-vapor explosion

BNL Brookhaven National Laboratory

C Celsius

CFR Code of Federal Regulations CGA Compressed Gas Association

SI-ITS Service Innovation-Institutional Training Services (group)

DOT Department of Transportation

F Fahrenheit

HPI human performance improvement

HVACR heating, ventilation, air conditioning, and refrigeration

IWD integrated work document

K Kelvin L liter

LAMC Los Alamos Medical Center LANL Los Alamos National Laboratory

LEL lower explosive limit LEV local exhaust ventilation

LP propane

MIE minimum ignition energy
MRI magnetic resonance imaging

NEC National Electric Code

NFPA National Fire Protection Association

NIST National Institute of Standards and Technology

OSH Occupational Safety and Health OSH-ISH Industrial Hygiene and Safety

OSH-OH Occupational Health

OSHA Occupational Safety and Health Administration
OS-PT Operations Support-Packaging and Transportation

P procedure

PPE personal protective equipment

psi pounds per square inch

psig pounds per square inch gauge

R Rankine

UEL upper explosive limit

# Module 1: Definitions, Examples, Properties, and Uses of Cryogens

#### **Module Overview**

**Note:** Unless specifically called out as different, the term "cryogen" will be used to refer to true cryogens and other liquefied gases [e.g., propane (LP) and CO<sub>2</sub>].

The safe use of cryogens requires that the user be familiar with the definitions and properties associated with cryogens. This module covers some of these definitions and also introduces some common cryogens, their uses, and properties. Additional definitions can be found in P101-5.

# **Module Objectives**

When you complete this module, you will be able to recognize

- definitions associated with cryogens; and
- examples of common cryogens, their uses and properties.

# **Definitions Associated with Cryogens**

Definitions associated with cryogens include the following:

**absolute zero**—the temperature at which a thermodynamic system has the lowest energy  $(-459.67^{\circ}F = -273.15^{\circ}C = 0^{\circ}R = 0 \text{ K})$ .

**boil-off**—inherent to the storage of a cryogenic liquid and refers to the vapors released when a liquid cryogen becomes gaseous from ambient heat infiltrating the storage vessel. The discharge of these vapors out of the storage container is called venting. Also see Normal Evaporation Rate (NER).

**boiling point**—the temperature at which the pressure exerted by the surroundings on a liquid is equal to the vapor pressure of the liquid. At a liquid's boiling point, the addition of heat results in the transformation of the liquid into its vapor state without raising the temperature.

**critical temperature**—of a substance is the temperature above which vapor of the substance cannot be liquefied, regardless of how much pressure is applied.

**critical pressure—**of a substance is the pressure required to liquefy a gas at its critical temperature.

**cryogen (cryogenic fluid)**—a substance that is a gas at room temperature and normal atmospheric pressure and that becomes a liquid at a temperature below 120 Kelvin (K) (i.e., has a boiling point below 120 K at normal atmospheric pressure). For reference, 120 K is -153.15°C, 216°R (Rankine scale), or -243.67°F.

**Dewar**—a thermally insulated, vented vessel designed to contain and maintain low boil-off loss of cryogenic liquids. Some Dewars are simple, open-mouthed, nonpressurized, vacuum-jacketed, or otherwise insulated vessels.

**expansion ratio (volumetric)**—the ratio of the volume change after a liquid cryogen is warmed from the normal boiling point to room temperature and local ambient pressure. At the extreme, liquid neon expands to 1445 times its original liquid volume at sea level and 1.445 \* 1.3, or 1879 times its original liquid volume at 7500 feet at 70°F (20°C).

**heat of vaporization**—the heat required for a unit mass in the liquid phase to convert to the gas phase. The heat of vaporization determines the insulation necessary to maintain the temperature at or below the boiling point.

**liquefied gas**—a substance with cryogen-like properties that becomes a liquid at a temperature above 120 K = -153.15°C = 216°R (Rankine scale) = -243.67°F.

**normal evaporation rate (NER)**—describes the amount of cryogenic liquid that boils off to vapor during a given period of time. Specific values are make and model dependent and are usually given as a %/day, liters/hour or liters/day. Also see boil off.

**normal temperature and pressure (NTP)**—a National Institute of Standards and Technology (NIST) standard set of conditions with a temperature of 20°C (293.15 K, 68°F) and an absolute pressure of 1 atm (14.696 psi, 760 Torr (mmHg), 101.325 kPa). Compare with STP.

standard temperature and pressure (STP)—a International Union of Pure and Applied Chemistry (IUPAC) standard set of conditions with a temperature of 0°C (273.15 K, 32°F) and an absolute



pressure of exactly 105 Pa (0.987 atm, 14.503 psi, 750.06 Torr (mm Hg), 100 kPa, 1 bar). Compare with NTP.

thermal expansion coefficient—a physical parameter that describes how the size of an object changes with a change in temperature. Specifically, it measures the fractional change in linear size per degree change in temperature at a constant pressure.

**trapped volume**—any element of a piping/vessel system, typically between two valves, that does not have a relief valve or rupture disk. **Note**: The pressure in a trapped or constant volume that is completely filled with liquid nitrogen can reach approximately 43,000 pounds per square inch (psi) when warmed to room temperature.

#### **Units of Measure**

The **units of measure** used to describe the temperature of cryogens are degrees Fahrenheit (°F), degrees Celsius (°C), degrees Rankine (°R), and Kelvin (K). To convert from

°F to °C: subtract 32, multiply by 5, and divide by 9;

• °C to °F: multiply by 9, divide by 5, and add 32;

• °C to K: add 273 (approximate); and

• °F to °R: add 460 (approximate).

At sea level, atmospheric pressure is 1 atmosphere (atm) = 14.696 psi, 760 Torr (mm Hg), and 101.325 kPa. Water boils at  $212^{\circ}F = 100^{\circ}C = 672^{\circ}R = 373$  K and freezes at  $32^{\circ}F = 0^{\circ}C = 492^{\circ}R = 273$  K.

#### **Lessons Learned**

#### **Cryogen Incident at Los Alamos National Laboratory**

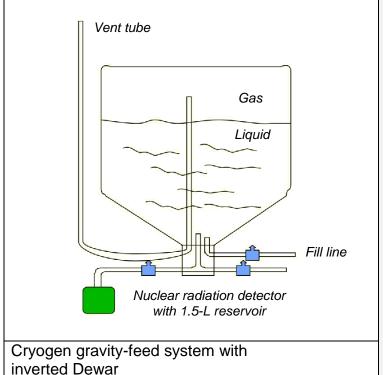
At LANL, a cryogen gravity-feed system with an inverted Dewar similar to one used at Sandia National Laboratories was designed and built to ensure a constant delivery of liquid nitrogen to a detector. The arrangement (see figure) was meant to reduce the overtime required during weekends and holidays to refill a small, 1.5-L reservoir that came with the detector. However, the personnel assigned to design and build the system had no formal cryogenic training.

After several unsuccessful attempts and some modifications, the liquid nitrogen system was finally filled. On Wednesday, December 23, 1992, at about 4:30 p.m., just before the start of the winter break and after the third successful fill, the technician left the system.

At 5:18 p.m. on that day, approximately 3 minutes after the office was finally vacated, the Dewar flask suffered a catastrophic overpressure failure (it blew up). Although no personnel were present, damages to equipment and facilities were estimated at \$35,000.

Analysis of the incident indicated that obstruction of a 3/8-in. vent line was the most likely cause of failure because thread marks, presumably from a bolt, were found in the end of the vent line. Subsequent interviews with personnel revealed that, after the modified system was filled, loud popping sounds similar to those made by a coffee percolator were heard several times throughout the day. The fabricated venting system resulted in considerable thermal contact between the outside air and the liquid nitrogen, causing it to boil very rapidly, which probably accounted for the popping. The noise may have prompted someone disturbed by it to insert a bolt into the vent line sometime after about 4:30 p.m.

Paraphrased from Liquid Nitrogen Dewar Explosion DP-ALO-LA-LANL-TA55-1992-0045



#### Contributing factors:

- poor management
  - no oversight was provided
  - unqualified personnel were assigned
  - lack of required training
- inadequate design
  - quick-fix approach used (which often does not work)
  - no account taken of possible pressure buildup
- warning indicators ignored
  - unsuccessful initial filling should have been enough to question the design
  - loud popping indicated rapid boiling and loss of cryogen

# **Properties of Cryogens**

Variations in the physical states of a cryogen can be observed by the attenuation of light transmitted through a vessel containing the substance.

Sublimation is the phase transition of a solid to a gas without passing through a liquid state. The critical point is the highest temperature and pressure at which fluids can have a liquid phase. The critical point depends on the material and has a pressure called the critical pressure and a temperature called the critical temperature. At temperatures above this point, a fluid cannot have a liquid phase, regardless of how much the pressure is increased. Just above the critical point, the density of a fluid changes very rapidly with both temperature and pressure, but there is no longer a distinction between gas and liquid. Properties of the substance can change dramatically when this point is reached. For instance, liquid water under normal conditions is nearly incompressible, has a low thermal expansion coefficient, has a high dielectric constant, and is an excellent solvent for electrolytes. Near the critical point, all of these properties change into the exact opposite: water becomes compressible, expandable, a poor dielectric, and a bad solvent for electrolytes and prefers to mix with nonpolar gases and organic molecules. At the critical point, only one phase exists. The heat of vaporization is zero.

Cryogens usually have very low critical temperatures. Above the critical temperature, the substance typically behaves like a gas in that it tends to occupy a closed volume completely. However, its density fluctuates between a liquid and a gas near the critical point (critical opalescence).

Some gases can be liquids at room temperature if the pressure is high enough and if their critical temperature is above room temperature [293 K (20  $^{\circ}$ C)]. Cryogens cannot be liquefied at room temperature at any pressure. Critical temperatures and boiling points of some cryogens and cryogen-like materials are shown in Table 1.

Table 1. Critical Temperatures (Tc) and Normal Boiling Points (TB)
of Cryogens and Liquefied Gases

or or yogono and indicate according						
Name	T <sub>C</sub> (K)	T <sub>B</sub> (K)	Name	T <sub>C</sub> (K)	T <sub>B</sub> (K)	
Helium-4	5.2	4.2	Methane (CH4)	190	111	
Hydrogen	33	20	Krypton	209	120	
D2	38	24	Ozone*	261	162	
Neon	44	27	Xe*	290	165	
СО	133	68	Ethylene (C2H4)*	232	169	
Nitrogen	126	77	Ethane*	305	185	
F2	144	85	Carbon dioxide*	304	195	
Argon	151	87	Propane*	370	231	
Oxygen	155	90	Chlorine*	416.9	239.11	
Liquefied natural gas	190	111	Ammonia*	405.5	239.81	

<sup>\*</sup>Liquefied gas (T<sub>B</sub> > 120 K)

Cryogens expand dramatically when they vaporize and are warmed to room temperature. Because LANL is at an altitude of ~7500 feet, the expansion ratio must be adjusted for ambient temperature and pressure as follows:

$$ER_{ambient} = ER_{NTP} * \left(\frac{760 \, mm \, Hg}{P_{ambient}[mm \, Hg]}\right) \left(\frac{273 + T_{ambient}[C]}{T_{NTP}[K]}\right) ,$$

where

$$P_{ambient}^{\dagger}$$
 ~ 584 mm Hg (0.77 atm) at  $T_{NTP}$  = 20°C = 298 K.

$$ER_{ambient} = ER_{NTP} * (1.30)$$

†http://www.altitude.org/air\_pressure.php.

If a cryogen is not allowed to vent, very high pressures can be created. Table 2 shows some examples of the pressures that would result in a sufficiently strong vessel completely filled with a cryogenic liquid that was not allowed to vent and warmed to room temperature (i.e., 300 K).<sup>†</sup>

Table 2. Potential Pressures of Unvented Cryogens Heated to Room Temperature Gases

Gas	Pressure (in psi)		
Helium	15,000		
Hydrogen	25,000		
Nitrogen	43,000		

† F. J. Edeskuty et al., see References.

Table 3 outlines various physical parameters for 11 cryogens and 6 liquefied gases.

Table 3. Approximate Physical Parameters of Common Cryogens and Liquefied Gases

Cryogen or liquefied gas	Notes	Expansion Ratio @ NTP	Expansion Ratio @ Ambient	Boiling Point (BP) at 760 mmHg	BP Density (kg/m3)	Heat of Vaporization @ BP (kJ/kg)
Helium	Inert cryogen but can condense oxygen out of air	737.4	959	4.22	125	20.42
Hydrogen	Flammable cryogen	831.2	1081	20.40	71	446
D2	Flammable cryogen	962.6	1252	23.70	163	301
Neon	Inert cryogen	1415	1840	27.10	1205	86
Nitrogen	Inert cryogen but can condense oxygen out of air	680.4	885	77.30	809	199
СО	Flammable cryogen	669.4	871	81.70	792	216
F2	Reactive cryogen	934.3	1215	85.00	1502	175
Argon	Inert cryogen	825.5	1074	87.30	1393	161
Oxygen	Cryogen oxidizer	843.6	1097	90.20	1141	213
Methane (CH4)	Flammable cryogen	621.4	808	111.60	423	512
Krypton	Inert cryogen	680.5	885	120.00	2400	108
Xe	Inert liquefied gas	526.9	685	165.00	3040	96
Ethylene (C2H4)	Flammable liquefied gas	475.5	619	169.40	568	482
Carbon dioxide	Inert liquefied gas	845	1099	194.65	1562	571.3
Propane	Flammable liquefied gas	305.9	398	231.15	580.88	356
Chlorine	Reactive liquefied gas	521	678	239.18	573	288.1
Ammonia	Reactive liquefied gas	935.6	1217	239.65	682.6	1370

# **Uses of Cryogens**

A superconductor is a material that experiences a nearly total loss of electrical resistivity below an achievable temperature. Examples of materials that can be made into superconductors include iridium, lead, mercury, niobium, tin, and tantalum.

Because of their unique properties, cryogens are used in a variety of industrial and research applications. Some examples are to

- cool equipment and systems used in activities that require operation at low temperatures, such as supercomputers, highpower lasers, x-ray fluorescence systems, infrared cameras and telescopes, and scanning electron microscopes or scanning tunneling microscopes;
- slow atoms and molecules for the study of the behavior of materials at cryogenic temperatures. Some materials exhibit superconductivity; and
- provide researchers with large quantities of certain gaseous materials more economically and in less space. Often gases can be easier to handle, store, and transport as cryogenic liquids than as compressed gases just because of the smaller volume needed. For example, liquid nitrogen takes about one-fifth the space needed to store the equivalent amount of compressed nitrogen gas.

Biological and medical cryogen uses include

- cryosurgery and cryotherapy;
- cryo-cooling to provide epidermal protection during certain laser treatments;

# Module 1: Definitions, Examples, Properties, and Uses of Cryogens

- research with cryo-ablation to correct heart arrhythmia by creating lesions in the heart wall;
- refrigeration and storage of cells for biological research;
- · refrigeration of sperm for reproductive purposes; and
- magnetic resonance imaging (MRI), which uses superconducting magnets for medical diagnostic purposes.

The Spatial Infrared Imaging Telescope III (Spirit III) was designed with a sophisticated sensor system to measure various characteristics of celestial objects and upper atmospheric phenomena. The sensor system was designed to be cooled to cryogenic operating temperatures with a solid-hydrogen cryostat, the first of its kind to be used in space.



# **Module 2: Cryogen Hazards and Controls**

#### **Module Overview**

Incidents involving cryogens can result in personnel injury or death, equipment damage, and operational and facility shutdown. This module addresses common hazards and controls associated with the use of cryogens. By applying this knowledge and using the controls presented here, you can reduce the risk of unwanted events and avoid emergencies.

Listed below are general hazards and controls encountered when working with cryogens. Additional site- or task-specific hazards and controls exist but are not covered in this training.

# **Module Objectives**

When you complete this module, you will be able to recognize the following hazards and controls associated with cryogens:

- Over-pressurization;
- flammability;
- condensation;
- hot and cold thermally induced mechanical stress;
- embrittlement;
- exposure, including oxygen deficiency, toxicity, physical contact, and noise; and
- Dewar selection, use, and transport.

# **Hazards Associated with Cryogens**

#### **Pressure Hazards**

Room-temperature air surrounding a Dewar can effectively act as an unlimited source of thermal energy and can be easily absorbed by a cryogen. As the liquid is steadily heated, the vapor pressure of the liquid increases until it boils. If heating continues, the pressure and temperature will eventually rise past the critical point, and only the vaporized fluid will be present.

Liquid nitrogen (in a container without pressure relief devices) that is heated from its boiling point (77 K) to room temperature (293 K) could generate a pressure of almost 45,000 psi. The amount of stored energy suddenly released from a rupturing 1-m<sup>3</sup> container at this pressure is comparable to a 2-ton truck traveling 1920 mph or the energy released by detonating 324 lb of TNT!

Containers for cryogenic liquid storage or transport are designed to minimize heat transfer and allow for adequate venting. The heat that does reach the liquid causes the cryogenic liquid to boil off. The consequent rate of pressure buildup is determined by the

- heat of vaporization of the cryogen,
- heat transfer rate, and
- capacity of the system to vent.

If the containment system holding a cryogen does not allow for sufficient expansion or pressure relief, over-pressurization can occur. Over-pressurization can result in

- · serious injury or death,
- equipment and/or facility damage in the area of the containment system, and
- an explosive pressure release known as a boiling-liquid expanding-vapor explosion (BLEVE).

Causes of over-pressurization include improper system design and frost blockage of venting ports (i.e., ice plugs), which can lead to trapped volumes.



Over-pressurization can result in an explosive pressure release (BLEVE).

#### **Explosive Pressure Release**

If a large amount of heat is suddenly applied to a cryogenic liquid, flash vaporization may occur. In such cases, the vaporization and expansion of the cryogenic liquid, a BLEVE, are so fast that the phenomenon is similar to an explosion that results from extremely rapid combustion. Such a condition may occur when pressure on a saturated liquid at its boiling point is suddenly released, such as from a ruptured containment system.

Most liquefied flammable gas BLEVEs occur when containers are about one-half to three-quarters full of liquid. In extreme cases, container pieces have been observed to be propelled as far as 1/2 mile. Deaths from container fragments have occurred up to 800 feet away and from burns as far as 250 feet away from large (several cubic meters) containers. Because a cryogenic BLEVE exhibits a comparable rate of energy release, many of the hazards involved with combustibles are also present when cryogens are used.

#### **Propane Tank BLEVE**

On the morning of June 27, 1993, at 9:02, the Warwick Volunteer Fire Department responded to a report of a barn fire. When they arrived at approximately 9:21 a.m., the fire department found a large cattle barn ablaze. During the size-up phase, a 4000-L (1055-gal.) propane (LP) tank was found close to the barn. The relief vents were operating on the tank, shooting flames more than 5 m (16 ft) into the air. Firefighters began to apply water to the exposed LP tank in an effort to cool it. Suddenly the tank BLEVE'd and split into two large pieces. The blast sent one of the pieces into an open field, while the other piece traveled over 45 m (150 ft) and struck a fire truck and continued another 230 m (754 ft), where it struck a vehicle parked on the road, trapping an occupant.

Three firefighters were killed when the tank piece struck the truck, where they were donning protective equipment and preparing hose lines. The fourth firefighter was killed when he was thrown approximately 45 m (150 ft) as the LP tank part slammed into the truck. The blast injured three additional firefighters, as well as four civilians, including an occupant of the vehicle on the road.

www.nfpa.org/research/Fire\_Investigation/Alert\_Bulletins/BLEVE/bleve.html



#### **Pressure Hazard Controls**

Cryogen pressure hazards can be mitigated through the use of pressure-relief devices and by implementing safe work practices. Cryogen containment systems rely on redundancy (more than one device) and diversity (devices based on different mechanisms) to minimize the risk of excessive pressure. Pressure-relief devices must be provided for any areas in the containment system where cryogenic fluid or liquefied gas can be trapped.



Pressure relief often consists of an adjustable, spring loaded pressure relief valve (see above) and a rupture valve (see left) for backup in case the relief valve fails to function when needed. The relief pressure should marked, or tagged, on the valves. Figure 1 shows a generic cryogen containment system with pressure-relief devices installed at every location where gas pressure might build up to dangerous levels. These locations include the

- vacuum space between the inner and outer walls of the Dewar,
- cryogen bath space,
- · experimental volume, and
- piping or tubing between two cutoff valves.

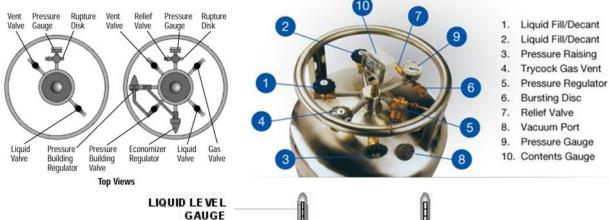
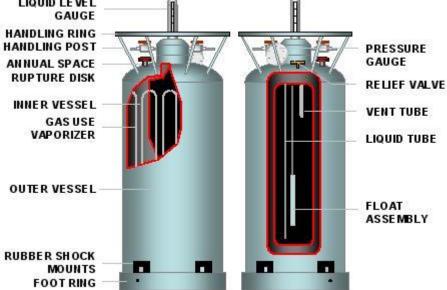


Figure 1. Locations of required pressure-relief devices.



When you are positioning pressure-relief devices, consider the direction of exhaust so that

 vent paths are directed away from personnel, critical equipment, and designated work areas (remember to consider the ricochet off surfaces and objects that would be redirected back toward equipment and workers); and

 devices on containment systems in poorly ventilated areas are connected to vents that release gases safely.

**Note:** Hydrogen vents should never release gas where contact with workers, equipment, and structures can occur or where gas can accumulate, such as in enclosed rooms or below the eaves of buildings. However, vents designed to release frozen air, such as a vent on the vacuum jacket of a hydrogen Dewar, may open to the immediate area.

Other pressure controls that might be required are

- the use of caps, seals, or check valves to prevent condensation of moisture or air from entering and forming an ice plug,
- orifices to reduce flow rates, and
- dust caps for liquid transfer hoses.

The Pressure Safety Committee can help you design cryogen containment systems. To contact the committee, call Occupational Safety and Health (OSH) at 505-606-0295.

#### **Safe Work Practices**

Safe work practices that help to ensure the continued safe operation of cryogen controls include

- inspection and maintenance of system components;
- leak tests before system use and after maintenance, repair, or reconfiguration;
- purging of contents before maintenance, repair, or reconfiguration;
- procedures to address normal operations and emergency situations;
- training to address normal operations and emergency situations; and
- procurement constraints to ensure the suitability of materials used in cryogen containment systems.





#### **Dewars**

Typical containment systems for cryogenic liquids consist of an insulated container, or Dewar (N.B., not dewar) where the cryogen is stored; and associated delivery lines and pressure-relief devices. Dewars are thermally insulated vented vessels designed to contain cryogens. The design of Dewars and their performance specifications vary by manufacturer and is highly dependent on the cryogen to be contained, the volume of the Dewar and the intended application.



Cryogenic storage Dewars may take several different forms, including open buckets, flasks with loose-fitting stoppers, and self-pressurizing tanks. All Dewars have walls constructed from two or more layers, with a high vacuum maintained between the layers. This vacuum provides very good thermal insulation between the interior and exterior of the Dewar. Good Dewar design reduces the rate at which the contents boil away (this is referred to as the normal evaporation rate) and is usually given as a %/day, liters/hour or liters/day. For information on Dewar specifications and performance characteristics go to the Cryogenic Society of America, Inc.'s Cryogenic Buyer's Guide and search by manufacturer.



Precautions are taken in the design of Dewars to ensure that they safely vent the gas as it boils off. The simplest Dewars allow the gas to escape either through an open top or past a loose-fitting stopper to prevent the risk of explosion. More sophisticated Dewars trap the vapor above the liquid and hold it at moderate pressure. Increasing the pressure increases the boiling point of the liquid (up to the critical temperature), allowing the liquid to be stored for extended periods. Excessive vapor pressure is released automatically through safety valves.

The method of decanting liquid from a Dewar depends on its design. Simple Dewars may be tilted to pour liquid from the neck.



**Important:** use extreme caution when decanting to prevent spills and burns.

Self-pressurizing designs use the gas pressure in the top of the Dewar to force the liquid upward through a pipe leading to the neck.

The primary components of two small (<100 L) conventional cryogenic Dewars, including the vacuum regions and indications of the delicate support structure, are shown in Figure 2. The provision for pressure relief on these small Dewars is an input port that is never tightly closed.

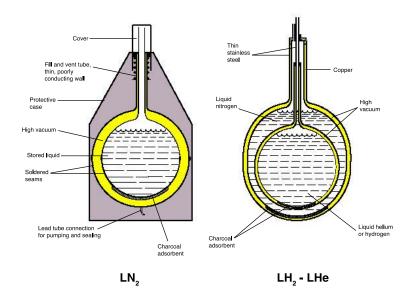


Figure 2. Examples of conventional cryogenic Dewars.

Figure 3 shows the overall design of a generic Dewar, which includes pressure-relief valves to prevent excessive pressures and a system of coiled pipes (pressurizing coils) between the inner and outer walls. This piping serves to control the pressure in the Dewar for purposes of extraction of the cryogen in either gaseous or liquid form.

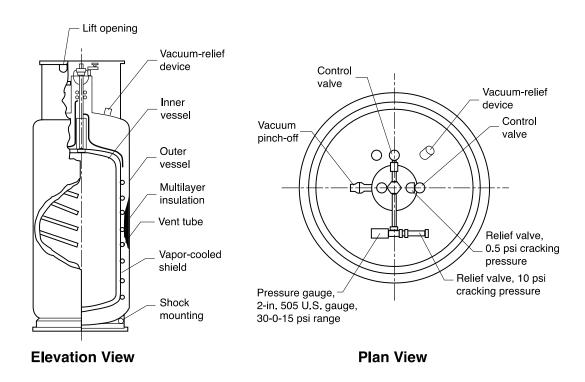


Figure 3. A generic pressurized Dewar.

Dewar volumes are often given in liters, but the gauges are usually marked in inches of liquid height. Therefore, it is convenient to have the volume calculation from the gauge reading; this conversion is as follows:

To get volume of liquid in liters, use the liquid level gauge reading in inches and multiply by

$$\frac{\pi \times diameter \, squared \, (in.^2)}{244 \, (\frac{in.^3}{l})}$$

Figure 4 shows a 160-L, pressurized, super-insulated Dewar, with the path of the coils going out of the insulated region to build up pressure in a controlled manner. The cryogen that boils as it circulates through the coils and exits as a pressurized gas also lowers the temperature in the space between the walls. Therefore, less radiant heat reaches the cryogenic liquid in the insulated region.

Extremely low-temperature Dewars for helium also have thin aluminized Mylar (superinsulation) in the vacuum region that helps to reflect any residual radiation.

- 1. Liquid valve
- 2. Economizer regulator
- 3. Vent valve
- 4. Burst disk (400 psig\*)
- 5. Pressure gauge
- 6. Pressure control valve (230 psig)
- 7. Pressure-building regulator
- 8. Pressure-building valve
- 9. Liquid level gauge
- 10. Gas use valve
- 11. Vacuum casing burst disk

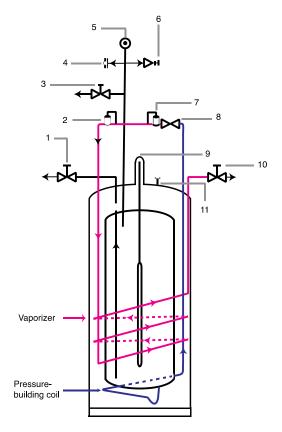


Figure 4. 160-L pressurized Dewar.

<sup>\*</sup>pounds per square inch gauge.

# **Human Performance Improvement**

Handling cryogens subjects the worker to a wide range of hazards. It is important to frequently reexamine existing activities, especially when they have not been done for a while. Carefully review the IWD(s) and get your questions answered and safety concerns addressed by management. This is especially important before beginning new operations.

Human performance improvement (HPI) is an approach used to address human error in the workplace. HPI treats human error as a symptom or a result of deeper problems within a system. One of the five basic principles of HPI is that people are fallible, and even the best make mistakes.

HPI recognizes two types of errors: active and latent. *Active errors* trigger immediate unwanted events. For example, a worker loses his/her balance and falls through a skylight. *Latent errors* result in unseen organizational weaknesses. Examples of latent errors include

- poor design
- gaps in supervision
- maintenance failures
- undetected manufacturing defects
- unworkable procedures
- clumsy automation
- shortfalls in training
- inadequate tools and equipment

Read the incident below and see if you can identify the active and latent errors.

#### **Dewar Top Ruptures and Injures Two Researchers**

A researcher transported a Dewar filled with shaved dry ice and vials containing small quantities of chemical and biological solutions to Brookhaven National Laboratory (BNL) via a commercial airline. The Dewar, actually a common coffee thermos, was almost 30 cubic inches in volume, with a screw-in top. The top was kept loose to allow venting of the dry ice gases during transport. The thermos was placed in a cold room upon arrival at BNL, the top unscrewed, the contents examined to ensure that sufficient dry ice remained to keep the contents cold, and the thermos top replaced by the researcher. Upon returning the next day to open the thermos, the researcher could not unscrew the top. The researcher did not observe an absence of frosting on top of the thermos, an indication that the thermos was not venting the dry ice gas. The researcher obtained assistance from a colleague, who used both hands to try to remove the top of the thermos while the researcher held the body of the thermos. During this attempt, overpressurization blew off the top of the thermos, which hit the researcher in the forehead. The body of the thermos hit the researcher's left thigh and thumb, while the colleague was sprayed with dry ice and suffered contusions on the left hand and knee.

Lesson ID: Y-1997-ER-CH-BNL-0001

#### **Module 2: Cryogen Hazards and Controls**

Question 1. What was the active error in this situation?

**Question 2.** What were the actual and potential latent errors in this incident?

Question 3. What would you do to prevent such an incident from occurring again?

Answers are on page 53.

For more information about HPI, register for *Human Performance for Workers* (COURSE 43428) through UTrain.

#### **Dewar Dislodged**

In the morning of January 28, 2011, gas plant personnel at LANL delivered a filled, 160-L argon Dewar to a caged area of the dock. Gas plant personnel left the argon Dewar in an upright position, still attached to the cart so that it could be moved to a manifold.

That afternoon an experienced chemical worker (W1) intended to move the recently filled Dewar a few feet to connect it to the building's gas manifold for laboratory use. As W1 attempted to stabilize the 160-liter Argon Dewar, it began to dislodge from the commercial transport cart. His right hand was caught between the Dewar and the cart, and the ends of his right ring and little fingers were severed. The Dewar fell onto the dock, and the transport cart fell to the parking lot below the dock.

A second worker (W2), walking into the building, observed that W1 was injured and transported W1 to LANL's occupational health (OSH-OH) facility. OSH-OH directed W1 to the Los Alamos Medical Center (LAMC) for treatment and evaluation. Medical personnel found that W1 had lost 2 centimeters (2 cm) from the end of his right ring finger and 1 centimeter (1 cm) from the end of his right little finger.

**Question 1.** What was the active error in this situation? *Failure to check equipment before moving it* 

**Question 2.** What were the actual and potential latent errors in this incident? *Manufacturing defects*, *shortfalls in training* 

**Question 3.** What would you do to prevent such an incident from occurring again? *Replace cart, train workers* 

#### LANL's Conclusions

Preliminary indications are that as W1 pulled back on the cart, either the pin in the adjustable assembly gave way, or the lifting stem became dislodged from the Dewar. According to instructions posted on the commercial transport cart, the hook height must be adjusted so that the hook is fully engaged through the lifting eye of the cylinder and in contact with the top of the eye before breaking over the cylinder. Once the hook height is adjusted, the truck is positioned to allow the hook to be engaged as the cart breaks over the cylinder.

Judgment must be made about the severity of an injury to determine whether the injured person should initially go to OSH-OH or the LAMC emergency facility. In this case, it may have been possible to attach the severed fingertips had they been recovered and surgery performed immediately at LAMC.

# **Cryogen Flammability Hazards and Controls**

Cryogens can present different fire danger based on their

- degree of flammability (e.g., for hydrogen and methane),
- increases in the range of flammability,<sup>†</sup>
- lowering of the minimum ignition energy (MIE) of the cryogen through changes in gaseous mixtures (e.g., oxygen and hydrogen), or
- the degree of air condensation from cryogenic cooling creating an oxygen-enriched environment (such as with hydrogenated compounds).

**Note**: A flammable cryogen will ignite only within a specific range of cryogen/oxygen mixtures. The flammable range lies between its lower flammability limit (a.k.a. the lower explosive limit, or LEL) and its the upper flammability limit (a.k.a. the upper explosive limit, or UEL) and is well determined for many flammable gases or vapors as a function of pressure. LELs and UELs are usually expressed as a volume percent.

Outside these flammability limits, a flammable cryogen does not normally pose a combustion hazard. Table 4 shows the flammability characteristics of five common cryogens.

Flammable cryogens once ignited can result in the creation of a deflagration or detonation wave. A deflagration is a rapid burn that travels at velocities at or below the local gas sound speed. If the ignited cryogen is confined without adequate venting, a detonation may occur. Detonations travel at velocities exceeding the local gas sound speed and are capable of much greater destruction.

Table 4. Flammability Characteristics of Five Common Cryogens

Gas	Nitrogen	Helium	Oxygen	Hydrogen	Methane
Explosive hazard with flammable mixtures	No	No	Yes	No	No
Explosive hazard with oxygen or air	No	No	_	Yes	Yes
Fire hazard type Flammable Promotes ignition	Nil No	Nil No	Nil <b>Yes</b>	Yes No	<b>Yes</b> No
Condenses air	Yes	Yes	No	Yes	No
Flammable range in air	_	_	_	4%–75%	5%–15%



The fire triangle.



#### **Cryogen Flammability Controls**

Oxygen, fuel, and heat (an ignition source) are required to initiate combustion, as illustrated by the fire triangle. To prevent unwanted combustion, one or more of the three components must be removed. Reduce the risk of cryogen flammability hazards with the following controls:

- identify and mitigate unwanted ignition sources:
  - consider the use of intrinsically safe or explosion-proof equipment, such as non-sparking motors;
  - ground electrical equipment in the immediate vicinity;
  - ground and bond vessels and transfer tubes together before transferring flammable cryogens from one vessel to another;
  - transfer flammable cryogens through closed, purged transfer lines; and
  - post "Flammable Gas" signs;
- prevent unwanted fuel-air mixtures as follows:
  - establish and maintain containment systems that are free of cryogen leaks from the system,
  - prevent the leakage of air or other gases into containment systems that hold flammable cryogen,
  - purge equipment with inert gas before and after use, and
  - establish and maintain a slight positive gauge pressure on the cryogen;
- remove nonessential combustible materials; and
- plan ahead for potential ignition incidents with appropriate gas monitors, alarms, fire control systems, and training as needed.

**Note:** The use of flammable cryogens in an area will require compliance with the National Electric Code (NEC) Standard National Fire Protection Association (NFPA) 70, Article 500, for all electrical equipment in that area, as specified in articles 501 through 510, which cover hazardous locations.

Minimum ignition energy (MIE) in air is the minimum spark energy that is needed to ignite the most easily ignitable concentration of fuel in air.

#### **Cryogenic Hydrogen Flammability Hazards**

Because of hydrogen's wide flammability range, low minimum ignition energy (MIE), and ability to damage the materials used in containment systems, hydrogen requires special controls. Figure 5 shows how pressure and concentration affect the MIE for hydrogen use. When the system pressure is increased, the MIE is lowered, indicating that high-pressure hydrogen is likely to be ignited more easily than low-pressure hydrogen. In the chart below, 28 kPa is about 4 Psi, and 101 kPa is 14.65 psi (about the atmospheric pressure at sea level. Note also that the MIE on the graph is in a logarithmic scale.

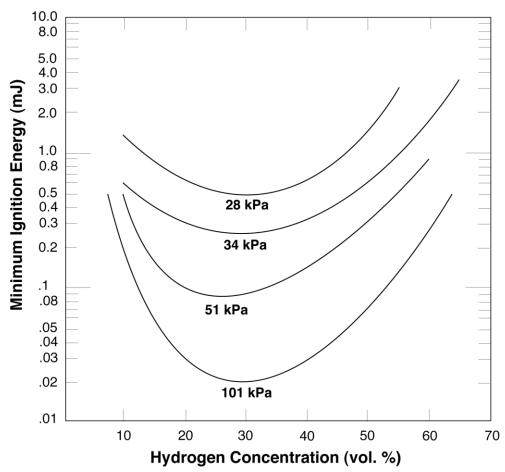


Figure 5. The effect of pressure and concentration on the ignition energy of hydrogen.

#### **Cryogenic Hydrogen Flammability Controls**

To minimize hazards caused by hydrogen gas leakage from containment systems,

 leak-test the containment system with helium under actual working conditions and temperatures;  consider the use of large-volume pressure-relief systems, but only as a control for deflagration;

**Note:** Pressure-relief systems are not considered adequate forms of control for a detonation because the magnitude and rate of pressure increase is too large to be handled by a mechanical device.

- inspect and maintain all shutoff systems (valve seats deteriorate over time and with usage); and
- install hydrogen detectors in situations where they are required, and use portable hydrogen gas leak detectors as needed.
   Contact OSH at 6-0295 to determine whether your work area requires air monitors.

**Note:** For more information, consult NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks.



Wall-mounted and portable hydrogen detectors.

#### **Cryogenic Oxygen Flammability Hazards**

Although oxygen itself is not a flammable gas, elevated levels of oxygen can significantly increase the flammability of other materials. Organic materials will be ignited more rapidly in an oxygen-enriched environment (>23.5% oxygen in air) because it will decrease the MIE and expand the flammability range, thereby increasing the risk of deflagration or detonation. Figure 6 shows how the flammability range of methane (CH<sub>4</sub>) increases as the oxygen concentration increases. For oxygen concentrations above 65%, the MIE needed to initiate methane combustion decreases below that of hydrogen (at normal oxygen concentrations).

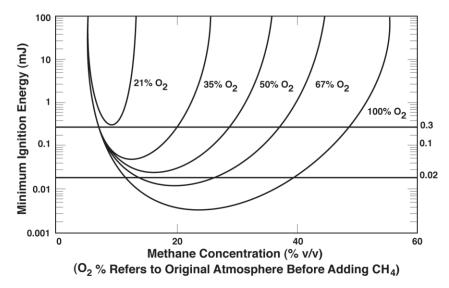


Figure 6. The effect of oxygen concentration on the combustibility range of methane concentration.

#### **Cryogenic Oxygen Flammability Controls**

Additional controls for flammability hazards created by oxygen include the following:

- Use only approved lubricants.
- Purge systems before performing maintenance, repair, or a reconfiguration.
- Post "Oxygen in Use—No Smoking" signs.
- Operate valves in oxygen service slowly to avoid the ignition of any contaminants that might be in the system.

# **Cryogen Condensation Hazards and Controls**

# **Cryogen Condensation Hazards**

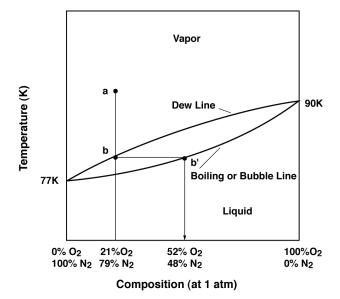
While contact between cryogens and a liquid or gas in a contained environment can sometimes be desirable (e.g., cold traps used to remove unwanted water vapor and CO2 from a system) poorly insulated cryogen systems coming into contact with the surrounding environment can result in some unexpected condensation hazards.

**Dew point** is the temperature and pressure at which a gas mixture begins to condense to a liquid.

Dry air is composed primarily of nitrogen (~78%), oxygen (~21%) and argon (~0.9%). Because they each have a different boiling point [nitrogen (77 K), argon (87 K), and oxygen (90 K)], exposure of air to any cryogen (e.g., nitrogen) that exists below the dew point temperature of air (82 K) will result in the air actually liquefying. Figure 7 shows that as the air condenses into a liquid the oxygen in the air tends to condense at a faster rate because of its higher

boiling point. The condensate that forms can have an oxygen composition as high as 52%, creating a potential oxygen-enrichment hazard. If the condensate forms on a combustible surfaces, such as asphalt, explosive conditions can be created.

Figure 7. Concentrations of oxygen and nitrogen in air vapor and air condensate.



When moisture in the air, or other gases such as carbon dioxide (195 K), are exposed to cryogens or ultra-cold surfaces they quickly condense and freeze, resulting in a buildup of frost and extremely cold liquids dripping onto surrounding surfaces.

If water or CO<sub>2</sub> freezes up in pipes or tubes it can result in a blockage, referred to as an "ice plug." If this blockage occurs in a venting system it can cause over-pressurization of the system.

In damp climates, frost that accumulates on containment system components helps prevent air condensation. The frost insulates the containment system from the surrounding air, reducing the possibility that the air will condense.

However, in areas where the humidity is generally quite low or with thin-walled, poorly insulated sections of pipe, frost formation is less likely to occur. In New Mexico, the relative humidity is often very low so that the likelihood of air condensation is higher than in damper climates while the formation of ice plugs is lower but not insignificant.

#### **Cryogen Condensation Controls**

To prevent or reduce the condensation of air and to protect workers and equipment from exposure to the extreme cold of the cryogen, consider the following controls:

- Where possible, use vacuum insulation.
- Insulate components with nonflammable insulation to prevent the external temperature of a cryogenic containment system from dropping below the dew point temperature of air (82 K).
- Use Dewars with exhaust lines and safety valve lines that are separated from each other to avoid thermal contact between the cold exhaust and the relief device.
- Place one-way (check) valves on exhaust lines to the atmosphere to prevent air from entering and condensing.
- Perform a leak test before evacuating cryogen baths, focusing on leaks by which air might be sucked into the cold part of the apparatus.
- Before beginning operations, purge and evacuate all equipment with an inert gas that liquefies below or at the anticipated cryogenic temperature.

# **Cryogen Thermal Stress Hazards and Controls**

#### **Cryogen Thermal Stress Hazards**

The components of cryogen containment and delivery systems often experience extreme differences in temperature that can create thermally induced mechanical stresses (i.e., thermal stress). Thermal stress hazards may be caused by

- the installation of a system component for which the length is constrained as the temperature varies.
- temperature differentials (gradients) across a material, and
- bonded materials with widely different thermal expansion coefficients

Thermal stress may occur between the inner and outer walls of piping materials or along the entire length of a piping system caused by non-uniform temperature gradients. These thermal stresses can easily exceed the design parameters of cryogen containment materials, making system failure likely. Thermal stress occurs under two circumstances: steady-state thermal stress and transient thermal stress.

A **gradient** is the rate of change of a parameter with distance, i.e., the change in the parameter over a very small distance divided by that distance.

#### Steady-State Thermal Stress

Steady-state thermal stress can occur during the normal thermal contraction of containment system materials from room temperature to cryogenic temperatures. The amount of steady-state thermal stress placed on a containment system depends on the temperature gradient within individual system components.

#### Transient Thermal Stress

Transient thermal stress can occur during the cool-down of cryogenic equipment from room temperature to operating temperature. Transient thermal stresses occur only as a containment system undergoes a temperature change. Transient thermal stress can occur in the following situations:

- A cryogen is pumped into a containment system too quickly. In this case, the system can cool too rapidly, causing overstress in thick sections, where large temperature gradients can occur.
- A cryogen flows into a containment system too slowly. In such a situation, it may be possible to overstress a horizontal piping system, particularly if plastic piping is used. The low thermal conductivity of the plastic results in large temperature gradients along the length of the pipe.

## **Cryogen Thermal Stress Controls**

The following controls are suggested to guard against thermal stress hazards:

- Contact the manufacturer to obtain the thermal expansion coefficients for the specific materials. Try and select materials with similar thermal expansion coefficients.
- Design transfer lines so that bends allow for expansion and contraction, as shown in Figure 8.

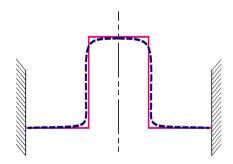


Figure 8. Design of transfer lines.

Thermal
conductivity is the
rate of heat flow
divided by area and
by temperature
gradient, i.e., it is
the heat flow per
unit area per degree
of temperature
gradient.

• Adjust flow rates in long transfer lines to minimize the time that large temperature gradients exist, as shown in Figure 9.

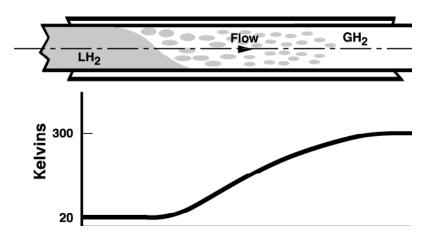


Figure 9. Cool-down model showing the gradual variation of phases of a cryogenic substance that causes longitudinal thermal gradients.

For help controlling thermal stress hazards, contact AET-1 DO, the OSH-ISH Cryogen Program (<a href="mailto:cryo@lanl.gov">cryo@lanl.gov</a>), or the OSH Division Office at 606-0295.

# **Cryogen Embrittlement Hazards and Controls**

Many materials become embrittled when they are exposed to extreme cold or exposed to hydrogen.

#### **Cold Embrittlement**

Toughness is the capacity of material to sustain impact without breakage.

Most materials increase in tensile and yield strengths as the temperature is lowered (see Figure 10 for aluminum and 430 stainless steel). However, at cryogenic temperatures, many materials become brittle and fracture, resulting in catastrophic failure of the material. The yield strength is defined as the stress at which permanent deformation occurs [i.e., the object will no longer return to its original dimension(s) after the load is removed]. Tensile strength is a measurement of the stress required to break apart an object as it is stretched.

For 430 stainless, the yield strength increases faster than the tensile strength, which causes a loss of ductility as the temperature decreases, making the material more brittle. At temperatures below ~222 K (–50°C), several materials, such as plastic, rubber, and carbon steel (i.e., ordinary steel), can become so brittle that relatively little impact energy will result in breakage and system failure (loss of toughness).

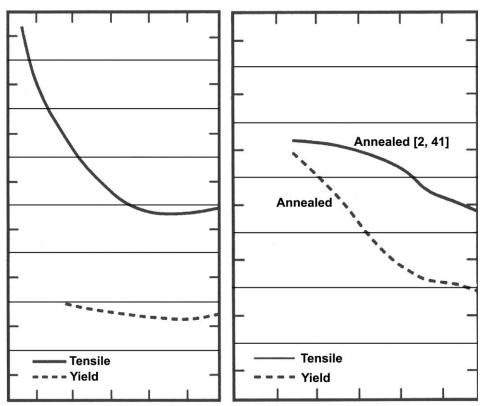


Figure 10. Tensile and yield strength vs temperature for aluminum (left) and stainless steel (right).

#### **Cold Embrittlement Controls**

To reduce the risk of system failure, select ductile materials that resist cold embrittlement (e.g., 300-series stainless steels, copper, and most alloys of aluminum). Ductility, the opposite of brittleness, is defined as the ability of a material to undergo permanent deformation due to tensile loading without fracturing.

Figure 11 shows how the ductility of several materials changes under various temperature conditions. At one extreme are 9% nickel steel and C1020 carbon steel, which undergo a dramatic decrease in toughness as the temperature drops from 200 K to 100 K. At the other extreme, 304 stainless steel actually becomes slightly more impact resistant as its temperature is reduced.

Liberty ships were produced in massive numbers to carry supplies to Europe during World War II. These ships were built with substandard steel and in sections that were joined together in as little as 1 week per ship. Unfortunately, cold embrittlement caused some ships to fracture and sink when they encountered the extreme cold (slightly below 0°C).

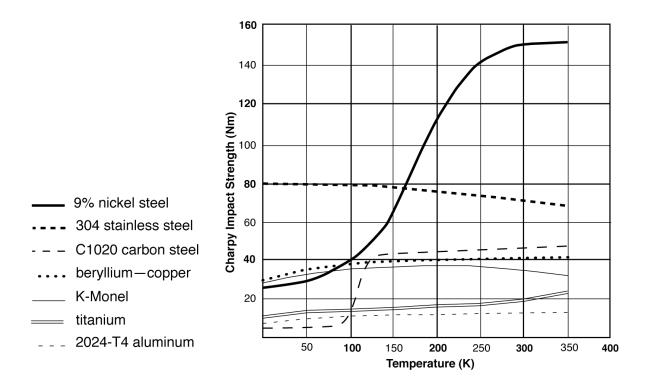


Figure 11. The effect of temperature on the impact strength (toughness of various materials).

# **Hydrogen Embrittlement Hazards**

Internal and environmental hydrogen embrittlement of cryogenic containment systems seems to occur in the range of 250 K to 350 K (i.e., -10°F to 170°F). Internal hydrogen embrittlement is the result of the introduction of hydrogen during the processing of the material, whereas environmental hydrogen embrittlement occurs when the material is placed in a hydrogen-enriched atmosphere.

A rough, fractured surface that appears brittle is an indication of hydrogen embrittlement. Figure 12 shows a fracture caused by hydrogen embrittlement. Some studies have indicated that hydrogen diffusion into steel is accelerated by contaminants such as arsenic, selenium, tellurium, antimony, and phosphorus.



Figure 12. Fracture caused by hydrogen embrittlement (The Hendrix Group).

# **Hydrogen Embrittlement Controls**

Hydrogen containment systems should be constructed only from materials resistant to hydrogen absorption. To reduce the risk of structural failure caused by contact with hydrogen, consider the use of stabilized 300-series stainless steels, copper, brass, and aluminum as materials for hydrogen containment system components.

# **Cryogen Dewar Selection, Use, and Transport**

#### **Selection and Use of Dewars**

Consider the following practices and precautions when selecting and using Dewars:

- Make sure the Dewar is clean and is designed for the cryogen for which it will be used. For example, the flask material of some Dewars may not be able to withstand the low temperature of liquid nitrogen.
- Follow the manufacturer's instructions on use, care, and maintenance.
- Before using glass Dewars, tape or enclose them in a protective housing to capture glass shards if the Dewar were to break.
   These steps will help prevent cryogenic burns.
- Periodically inspect vents to make sure they are not plugged.
- Do not subject a Dewar to sharp impacts or severe vibration. If you have reason to believe a Dewar has been damaged, remove it from service. Tag it as unusable.
- When you are transferring cryogens to or from Dewars, transfer the cryogen slowly to prevent splashing (i.e., prevent cryogenic burns) and to cool the receiving container gradually.

# **Transporting Dewars**

Consider the following practices and precautions when transporting Dewars:

- Seek assistance if you are not comfortable lifting or moving a Dewar. Many injuries that occur during cryogen operations result from sprains or strains from the handling of heavy, awkward equipment.
- For long distances, walk the path down to make sure it is clear.
   Note hazards, such as grates or large cracks, that could cause tipping, or obstacles that could impede progress.
- Move large Dewars (>30 L) with hand trucks designed to secure the Dewar to the hand truck. Do not "walk," roll, or drag large Dewars across a floor.
- Smaller Dewars (10 to 30 L) can be transported on top of a rolling table or dolly.

**Important:** As a result of a serious accident and injury, the Harper 600 carts are no longer approved for use as Dewar carts at LANL and should be taken out of service. The approved replacement is the Anthony 86U-4 cart.<sup>††</sup>

 Very small Dewars (<10 L) that have a provision to be carried by hand may be moved without a cart or rolling table; however, for a reactive cryogen such as oxygen, a cart or dolly is recommended, especially for extensive distances (>100 feet).

†† LANL Memorandum PADSTE:11-054.

- Wear eye protection when carrying a Dewar. Long pants and long-sleeve shirts are also required.
- Avoid clothing made from synthetics if you are transporting flammables or oxygen.
- Do not transport cryogens in open containers.
- If an elevator will be used during transport of a filled Dewar, do not accompany the filled Dewar within the elevator. Use the following procedure:
  - Work in pairs.
  - Place a sign on the Dewar that indicates "Cryogen Present— Do Not Enter" before putting it in the elevator.
  - Have one person send the Dewar and another wait to receive the Dewar at the floor destination.



Harper 600 Series Cart.



Anthony 86U-4 Cart.

Store cryogens in facility-approved locations. In general, cryogens should be stored

- in approved storage vessels having pressure-relief valves,
- in well-ventilated areas to prevent buildup of flammable gases or oxygen displacement,
- away from sources of ignition,
- in a manner that prevents or minimizes contact of moisture with storage containers to prevent ice plugging of relief devices, and
- in a manner that allows periodic inspection for ice plugging and other concerns.

# **Cryogen Health Hazards and Controls**

Health hazards associated with cryogen use include oxygen deficiency (i.e., asphyxiation), toxicity, physical contact, and noise.

Asphyxiation is suffocation resulting from a lack of oxygen.

# Oxygen Deficiency

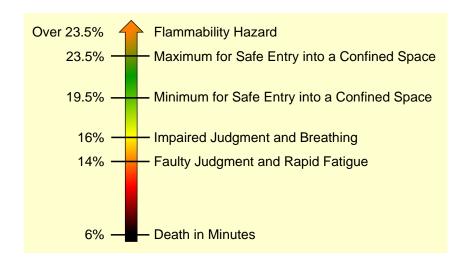
With the exception of liquid oxygen, all uncontained liquid and gaseous cryogens create local oxygen deficiency and can result in asphyxiation as they evaporate. As the escaped liquid warms, it turns to gas and expands rapidly, displacing breathable air and resulting in a lowered percentage of oxygen in the room.

At locations such as Los Alamos, where the local barometric pressure is much lower than at sea level, the effects are even more pronounced (the expansion of liquid cryogens increase by approximately 30%).

**Important:** Workers who enter areas where more than a small amount of cryogens (a few liters) are used without oxygen sensors must exercise extra caution to avoid unexpected oxygen deficient atmospheres and prevent asphyxiation. Do not use cryogens in an unventilated area. In general, if you spill, leave immediately and let others know that they should leave, as well.

The concentration of oxygen in normal air is about 21%. If the oxygen concentration rises above 23.5%, the risk of fire increases dramatically. Alternatively, if the oxygen concentration drops below 19.5%, the atmosphere presents a health hazard, the severity of which increases as the oxygen concentration diminishes. Signs and symptoms of oxygen deficiency are shown in Figure 13.

Figure 13. Signs and symptoms of oxygen deficiency based on the partial pressure of oxygen at sea level



Additional factors that affect personnel in low-oxygen environments include altitude, acclimatization, and individual susceptibility.

#### **Altitude and Acclimatization**

Although air contains approximately 21% oxygen at all livable elevations, the actual availability of oxygen varies according to partial pressure. Because the partial pressure of oxygen decreases as altitude increases, the high altitude of Los Alamos effectively decreases the amount of oxygen available to the body until a worker becomes acclimated.

Workers from lower altitudes who are not acclimated to the elevation of Los Alamos may be more susceptible to the effects of low oxygen concentrations. In Los Alamos (approximately 7,500 feet above sea level), the air is "thinner," so there is only 77% as much oxygen per volume of air as there is at sea level.

# Individual Susceptibility

Workers with respiratory problems may be especially susceptible to oxygen-deficient atmospheres. Reduced respiratory function can result from infections (influenza or pneumonia), health conditions (asthma, heart disease), lifestyle (smoking), or past exposure to airborne hazards (ammonia, silica, or asbestos).

#### **Oxygen Deficiency Controls**

Controls used to minimize the risk of oxygen deficiency include the following:

 Evaluate the workspace to determine the volume of cryogen that may safely be brought in. In some situations, a workspace

The initial acclimatization of workers who have just arrived from lower altitudes usually takes 1 to 2 weeks. During this time, the number of red blood cells used to transport oxygen within the body increases. A second form of acclimatization that takes longer is the opening of more air sacs (alveoli) in the lungs.

- evaluation by an industrial hygienist is required. See Module 3 and P-101-5, Section 3.3 for more information.
- Ensure adequate ventilation for all areas where cryogens are used. Documented evaluation and/or ventilation measurement by a qualified industrial hygienist may be necessary.
- Monitor the workspace periodically to ensure adequate atmospheric concentrations of oxygen. (If necessary, install a continuous oxygen monitor with alarms to permit timely warning and evacuation of workers if oxygen concentrations move above or below safe levels.)
- If the oxygen content falls below 19.5%, evacuate the workspace immediately, especially confined spaces.

## **Toxic Cryogens**

Unlike inert cryogens, toxic cryogens react chemically with the body. The toxic cryogens are fluorine and carbon monoxide.

#### **Fluorine**

Fluorine presents a hazard through inhalation or contact with the skin. Fluorine gas ranges from pale yellow to greenish in color and has a pungent, irritating odor; it is a strong oxidizer that will react with water to form hydrofluoric acid. Inhalation of fluorine gas can cause severe lung irritation.

Contact with hydrofluoric acid can result in permanent damage to the bones beneath the area of skin that was in contact with the acid. When fluorine is used, all personnel must be familiar with their site-specific emergency procedures for contact with fluorine. Such procedures may include calling 911, using a water wash or safety shower, and/or applying calcium gluconate, depending on the situation.

The affinity of carbon monoxide for red blood cells is much greater than the affinity of oxygen for red blood cells. This statement means that carbon monoxide will bind with red blood cells much more readily than oxygen and is difficult to remove.

#### **Carbon Monoxide**

Carbon monoxide is colorless, odorless, and deadly. Because it has such poor warning properties, workers can be exposed to dangerous concentrations of carbon monoxide without realizing it. Exposure to gaseous carbon monoxide causes asphyxiation by displacing oxygen in the body's red blood cells. Depending on the length of exposure and the concentration of the gas, exposure to carbon monoxide can cause adverse health effects, ranging from minor discomfort to death. When working with carbon monoxide, it is a good practice to assign at least two workers to the task, one of whom is to remain outside the space or area where carbon monoxide is being used. This person is to be an observer and be ready to summon emergency help if needed.

# **Toxic Cryogen Controls**

To minimize the risk of exposure to toxic cryogens,

- before introducing toxic cryogens into an area, verify the integrity of the delivery and containment systems by testing and purging vessels, pipelines, vaporizers, and controls at actual operational pressures and temperatures;
- ensure that ventilation is adequate and monitor workspaces where toxic cryogens are used;
- completely purge systems before maintenance, repair, or modification. Do not vent to an occupied space or where workers may accidentally enter;
- ensure that pressure relief devices do not vent to an occupied space or where workers may accidentally enter; and
- never work alone in areas where toxic cryogens are used.
   Ensure that at least one additional worker is positioned to monitor the activities from a safe distance and is able to summon assistance if needed.



# **Cryogen Contact Hazards**

Direct contact with cryogenic liquids or gases can freeze eyes or skin tissue and cause significant damage. The damage is sometimes referred to as a "cryogen burn" or a "cold burn" because intercellular ice crystals form between cells and draw water from within the cells, causing cell dehydration and damage that is similar to thermal burns. Most cryogen exposures are limited to causing eye and skin injuries, but in severe cases, hypothermia is a possibility.



Frozen skin appears waxy and yellow and is not initially painful; however, as the skin thaws, the victim feels significant pain. Thawing of the exposed area is accompanied by swelling and possible blistering. Dermal (skin) exposure to cryogens can occur through

- splashes or spills on the exposed skin;
- contact with the associated cold gas; or
- contact with cold items, such as uninsulated pipes or vessels containing cryogenic fluids.

Skin can survive a few seconds of cryogen contact because a protective vapor layer (Leidenfrost effect) is initially formed. However, longer contact will result in the skin freezing. Also, skin contact with extremely cold objects can result in attachment and will result in the skin tearing if workers attempt to forcefully separate themselves from the object.

Unlike the skin, eyes are particularly susceptible to serious injury because the fluids of the eye will freeze almost immediately upon contact with cryogens.

# are required by OSHA to know the following:when PPE is

cryogen hazards or for any other hazard, you

Whether you are wearing PPE for

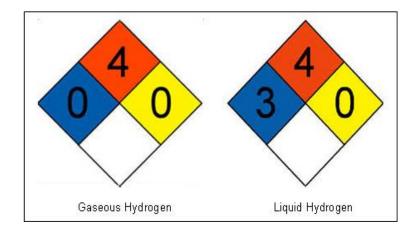
- necessary;what PPE is necessary;
- how to properly don, doff, adjust, and wear PPE;
- the limitations of PPE; and
- the proper care, maintenance, useful life, and disposal of the PPE.

# **Cryogen Contact Controls**

To minimize the risk of eye and skin contact with cryogens, consider the following controls:

- insulate all containment system pipes with nonflammable insulation;
- select shatter-resistant containers designed to hold the cryogen(s) that will be used;
- remove rings, watches, and similar types of jewelry before beginning work;

The NFPA Fire Diamond indicates the difference in health hazard between gaseous hydrogen and liquid hydrogen. See NFPA 704 for more information about these symbols.





- use care when handling cryogens (fill portable Dewars slowly, and place materials in cryogens slowly); and
- wear proper protective personal equipment (PPE), including
  - eye protection (safety goggles and a face shield when transferring from a storage vessel at a pressure higher than 7 psig into an open Dewar);
  - loose-fitting, insulated gloves (preferably without cuffs) that can be quickly removed if any cryogen spills onto them (gloves are not for protection from immersion and should not be exposed to liquefied oxygen);
  - cuffless pants that are worn outside of footwear rather than tucked into the tops of boots or shoes, to prevent cryogens spilled on the legs from running down into the boots;
  - covered shoes made with impermeable material and having no unnecessary openings; and
  - a cryogen apron (no leather should be used with oxygen), where splashing of liquefied gas is a potential cause for injury.

In a near miss involving liquid nitrogen, an employee was filling a 4-L Dewar. After stopping the flow of liquid nitrogen to check how full the Dewar was, the employee opened the liquid flow valve to continue filling. Restarting the flow caused the liquid nitrogen to splash out of the Dewar. Because the employee was not wearing eye protection, he was concerned that he had been splashed in the left eye, even though there was no evidence of a liquid nitrogen burn around the eye.

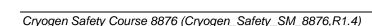
In another incident, an employee (who was not wearing gloves) received frostbite equivalent to first- and second-degree thermal burns to her left hand when she tried to shut the liquid flow valve on a 200-L liquid nitrogen cylinder after filling a 4-L Dewar bottle.

Paraphrased from Lawrence Berkeley National Laboratory Lessons Learned, LL-2002-02

#### **Cryogen Contact First Aid**

In the event of a serious cryogen burn to the skin, call 911 or SEO-EM: Emergency Management (667-6211) for medical assistance as soon as possible. Consider these first aid measures while awaiting advanced medical care:

- Remove the victim from the source of the cold.
- Be mindful of reduced oxygen levels in the area as the cryogen warms. If possible, increase ventilation by opening doors and windows or preferably move the injured worker to a different location.



- If safe to do so, gently remove (or cut away) any clothing that may interfere with the circulation of blood to the frozen tissues.
   Do not remove frozen gloves, shoes, or clothing.
- Do not rub the affected area(s) or break any blisters.
- Do not expose affected body parts to temperatures above 112
   °F, such as a heater or a fire.
- Do not immerse the injured area in water.
- Do not immerse the person in warm water. Rapid warming can cause heart arrhythmias.
- If hypothermia is possible, warm the person's trunk first, not the hands and feet. Warming extremities first can cause shock.

**Note:** Do not use safety showers, which are usually very cold and may worsen a possible hypothermic reaction. Furthermore, the flow rate may be sufficiently high to damage frozen skin.

- If the frozen tissues thaw before medical professionals arrive, cover the affected area with dry, sterile dressings and a large, bulky protective covering.
- If possible, make the patient comfortable. To prevent shock, move them off the floor and loosely cover their body, head, neck, and extremities with a blanket. Give the person a warm drink (no caffeine) if conscious.

**Note:** Health-related thermal stress (heat and cold stress) hazards and controls are presented in greater detail in Thermal Stress Awareness (Course 18649), a self-study course available through UTrain.

#### Noise

Long-term exposure to noise above 85 dBA will damage your hearing. The noise level of rapidly pouring or venting cryogens can easily exceed 100 dBA (much like the sound of a gas lawn mower from 3 feet away). Therefore, the sound pressure is approximately five times greater than long-term, safe exposure levels.

In some cases, quiet valves can be used; however, hearing protection for personnel working near cryogen filling or venting operations may be required and is highly recommended. Your deployed industrial hygienist can determine the noise levels in the area where you work. You can also contact the OSH Division Office.

Hypothermia is a life-threatening emergency in which the body's core temperature drops and the body can no longer keep itself warm. It is a condition similar to shock and should be treated as such.



The use of valves designed to reduce venting noise should be considered if noise is a concern.

# Module 3: Cryogen Agencies, Standards, and Procedures

#### **Module Overview**

Several external organizations oversee the safe use of cryogens in the workplace, and LANL also has procedures for its safe use. LANL has established support organizations to keep its workers safe. Included in this module is information about these organizations and a summary of safety guidelines that workers should follow.

# **Module Objectives**

When you complete this module, you will be able to recognize

- organizations and standards that affect cryogen use,
- LANL documents that affect cryogen use,
- cryogen-related roles and responsibilities of LANL support organizations and individuals,
- required evaluations for cryogen operations,
- warning signs of hazardous cryogenic conditions,
- general emergency response for cryogen accidents and incidents, and
- whom to contact for cryogen information or assistance.

# **Organizations and Standards That Affect Cryogen Use**

Organizations that establish standards and publish guidelines for the safe transportation, storage, and use of cryogens include the

- Compressed Gas Association (CGA) and
- National Fire Protection Association (NFPA).

Agencies that establish regulations for the safe transportation, storage, and use of cryogens include;

- the Department of Transportation (DOT) and
- the Occupational Safety and Health Administration (OSHA).



## **Compressed Gas Association (CGA)**

The CGA (<u>www.cganet.com</u>) has been dedicated to developing and promoting safety standards and safe practices in the gas industry since 1913. Its mission includes cooperation with federal, state, and local governmental departments and regulatory agencies in developing responsible regulations for industry.

NOTE: Materials from the CGA (see References) are available to CGA members. For CGAnet.com, LANL has five seats. The following individuals can obtain materials for you: CPSO (Ari Ben Swartz, <a href="mailto:abswartz@lanl.gov">abswartz@lanl.gov</a>, 606-2279), IHS (Tim Lopez, <a href="mailto:timlopez@lanl.gov">timlopez@lanl.gov</a>, 500-6625), and Gas Facility (Roberto Trujillo, <a href="mailto:(roberto t@lanl.gov">(roberto t@lanl.gov</a>, 665-1003), (Peggy Trujillo, <a href="mailto:peggyt@lanl.gov">peggyt@lanl.gov</a>, 665-7250), and (Jose Abeyta <a href="mailto:joea@lanl.gov">joea@lanl.gov</a>, 667-1118)..



## **National Fire Protection Association (NFPA)**

The NFPA publishes a wide variety of health and safety information and national consensus standards, some of which address the storage and handling of cryogens in the workplace (see References).

NFPA information and Standards may be obtained from either the LANL Research Library (<a href="http://int.lanl.gov/library/">http://int.lanl.gov/library/</a>) through the IHS Standards Expert or the IHS Engineering Workbench; they can also be purchased directly from NFPA (<a href="http://www.nfpa.org">http://www.nfpa.org</a>).



#### **Department of Transportation (DOT)**

The DOT creates regulations designed to ensure that the movement of hazardous materials on public roads is safe. The DOT regulations that address the packaging, labeling, and shipment of hazardous materials can be found in 49 Code of Federal Regulations (see References). In most cases, personnel at the LANL gas facility are responsible for the packaging and transportation of cryogens at LANL. Personnel who need to transport cryogenic liquids on public roads must be familiar with applicable DOT regulations and must have the required training.

**Note**: Training that addresses DOT requirements can be found through UTrain or by contacting Central Training Service Innovation-Institutional Training Services (SI-ITS) at the White Rock Training Center at 667-0059.

# **Occupational Safety and Health Administration (OSHA)**



Cryogen-related OSHA regulations address the use of compressed gases, hydrogen, oxygen, hazard communications, and the occupational exposure to hazardous chemicals in laboratories for personnel who work with hazardous chemicals. Standard 29 CFR 1910.1450 is a general approach to working with any chemicals at LANL. These standards and all other OSHA regulations are available online at <a href="http://www.osha.gov">http://www.osha.gov</a>. Hazard communication at LANL is addressed in <a href="http://www.osha.gov">P101-14</a>, Chemical Management.

# **LANL Procedure for Cryogen Use**

LANL <u>P101-5</u>, *Cryogens*, directly affects cryogen activities at LANL. Some of the provisions and requirements within this procedure include the following:

- General control requirements must be implemented for all cryogen use at LANL.
- The contents of all cryogen-handling systems must be labeled.
- Remember to monitor progress and check for liquefied oxygen entrapment while recharging or filling Dewars.
- Specific control requirements must be met before work is performed with liquid oxygen, flammable cryogens, and/or carbon monoxide.
- Specific training and qualification requirements must be met before personnel work with cryogens.
- Emergency response procedures for cryogenic operations must be written, posted at the entrance to the area, and made part of the appropriate integrated work document (IWD).
- Cryogenic pressure vessels shall be designed with American Society of Mechanical Engineers (ASME) codes using potential fault pressures (such as from cryogen boil-off) as the maximum allowable working pressure.
- Select materials that will resist cold embrittlement and stresses from differential thermal contraction (including those from rigid supports).
- Install pressure-relief devices in every space where liquid cryogen or cold gas could be trapped or where ice buildup could cause blockage and consequent pressurization. These spaces include the insulating vacuum space of cryostats containing a cryogen that may leak into that vacuum and pressurize it. Relief devices must be designed for cryogenic service if required.

- Select cryogenic piping that permits thermal contraction and condensation.
- Implement procedures to reduce the risk of water or air ice plugging. Before beginning cryogen operations, consult with AET-1, 667-8091; Dallas Hill at <a href="mailto:hill\_dallas@lanl.gov">hill\_dallas@lanl.gov</a> or 667-4240 is currently the appropriate contact.
  - If an ice plug does occur, *do not* attempt to remove the plug unless you are specifically trained to do so because the process is extremely dangerous if done incorrectly.
- Pressure-relief devices in corrosive service must be checked and calibrated every 2 years; those in noncorrosive service must be checked and calibrated every 5 years. Rupture or frangible disks and relief valves must be visually inspected every 2 years and replaced according to the manufacturer or every 15 years, whichever is less.

# **Roles and Responsibilities**

<u>P101-5</u> also presents roles and responsibilities for individuals and organizations who work with or support work with cryogens at LANL. Some of the roles and responsibilities are as follows:

# **LANL Support Organizations**

The following LANL support organizations have cryogen responsibilities:

- Mechanical and Thermal Engineering (AET-1): assists with a review of hazards, controls, calculations, and system design and engineering for new and existing cryogen systems and storage areas.
- Occupational Safety and Health (OSH): assists with the determination of hazards and controls, including ventilation, safe room volume determination, and operations involving liquid oxygen, toxic, flammable, explosive, or reactive cryogens.
- Operations Support-Packaging and Transportation (OS-PT)
   Gas Facility Team: is responsible for cryogen purchase and delivery and for the maintenance and inspection of portable liquid helium storage Dewars.

# **Responsible Line Managers**

Responsible line managers must ensure that

 LANL-designed systems that contain or use cryogens are designed according to good engineering practices;

- new cryogen cylinders, Dewars, and piping are inspected before use and on a regular basis;
- large cryogenic systems and associated engineering controls, such as ventilation systems and pressure-relief valves, are maintained;
- sensors or monitors for cryogens are calibrated and maintained in accordance with the manufacturer's instructions; and
- workers are trained and qualified to work with cryogens.

## **Cryogen Users**

Responsibilities of cryogen users include the following:

- Complete required training (i.e., this course and site-specific training) before performing cryogen operations.
- Obtain services from AET-1 for the proper design of cryogen systems.
- Send an e-mail to <u>cryo@lanl.gov</u> or contact OSH-ISH (606-0295) for the following:
  - Calculation or verification of calculations performed to determine the amount of cryogen that can be used safely for a specific operation or stored in a particular location.
  - Evaluation of new operations and significant changes to existing operations, including determining the adequacy of heating, ventilation, air conditioning, and refrigeration (HVACR); local exhaust ventilation (LEV), placement, and type of monitoring equipment and other controls for the work area; and if additional controls are required.
  - Review of operations when liquid oxygen, toxic, flammable, explosive, or reactive cryogens or their boil-off gases will be stored or used.
- Use carbon monoxide sensors or monitors when carbon monoxide is used or stored.
- Include emergency response requirements in the IWD or procedure for the cryogen operation.
- Maintain documentation relevant to the cryogen operation (e.g., designs, OSH-ISH evaluations, engineering reviews, and procedures).
- Consult <u>P101-5</u> Cryogens before beginning cryogen-related work.

# **Evaluation of Cryogen Operations**

OSH-ISH
personnel can
assist in preparing
written procedures
where inert
cryogen use or
storage is
anticipated. These
procedures may
be part of an IWD.

Before beginning operations with cryogens, all necessary evaluations required by P101-5 must be performed. To minimize delays in the project startup, try to have the necessary evaluations performed during your project's initial planning stages. This action will allow time to purchase any monitoring equipment and design any control systems deemed necessary by the OSH-ISH evaluation.

Knowledgeable and experienced personnel who are familiar with cryogen operations and safety requirements are responsible for preparing *procedures* before working with cryogens. IWDs may also be necessary to provide workers with clear procedural guidance that, if followed, will help minimize the risks associated with a task.

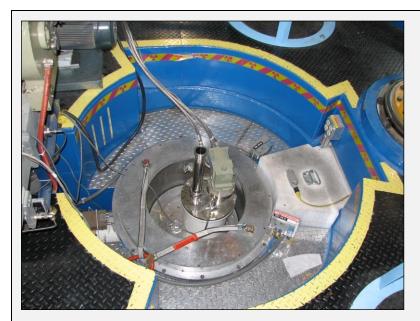
## **Lessons Learned**

#### **Over-Pressurization of Displex Cryostat**

In September 2008 at approximately 1040 hours, Researcher 1 (R1) attempted to remove the sample stick from a top-loading Displex cryostat base cylinder unit in preparation for a sample change. Initially, R1 warmed the sample from 15 K to 170 K. R1 then loosened the clamp, holding the sample stick in place, and noted that the sample stick was stuck. R1 turned away from the equipment for approximately 20–30 seconds to turn off the compressor used to cool the unit. Subsequently, the instrument researcher heard a loud popping sound. Turning back toward the cryostat, R1 observed that the sample stick was no longer in the unit. R1 then noticed a 3-inch hole in the sheet rock ceiling about 20 feet above the Displex unit. R1 was not injured.

This cryostat is an unmodified commercial top-loading unit designed to bring a variety of sample materials down to low temperatures (15 K) for neutron-scattering experiments. The unit is equipped with both a pressure-relief valve and pressure gauge, neither of which indicated an overpressure situation at the time of the event. The most likely cause of the event was an air leak into the sample volume while the sample was cold, leading to an internal buildup of frozen air trapped behind an air or ice blockage. Subsequent sample warmup then caused the frozen air to re-vaporize and expand at the bottom of the sample well, isolated by the blockage from both the pressure gauge and relief valve. A possible cause for the postulated air leak was a bad seal of the cryostat sample stick to the base unit. Sample sticks wear out quickly and must be replaced frequently.

Paraphrased from NA-LASO-LANL-ACCComomPLEX-2008-0006





Over-pressurization ejected a sample stick from a cryostat unit, creating a 3-inch-diameter hole (indicated by a broomstick handle) in the sheet rock ceiling about 20 feet above the unit.

## **Operations Requiring an Industrial Hygiene Evaluation**

Cryogen work that poses a risk to the health and safety of workers, the public, or the environment may require an evaluation by an industrial hygienist and/or the OSH-ISH Cryogen Program (cryo@lanl.gov).

An OSH-ISH cryogen evaluation *is required* for all operations in which any of the following conditions exist:

- the existing ventilation level has not been shown to meet or exceed <u>P101-5</u> requirements,
- the location does not have a ventilation-failure monitor.
- the location lacks an oxygen monitor, or
- the maximum amount of cryogen in use or stored in the location is greater than the level allowed by OSH-ISH.
- the amount of cryogen in use or stored in an occupied space is greater than V<sub>s</sub>.

## The Safe Volume Formula for Inert Cryogens

The safe volume formula is a quick and conservative way to estimate the maximum amount of a **single inert cryogen** that can be brought into a workspace without consulting an industrial hygienist or the OSH-ISH Cryogen Program (<a href="mailto:cryo@lanl.gov">cryo@lanl.gov</a>; see Section 3.3 of P101-5, Cryogenic Liquids or Cryogens).

For activities that require two or more cryogens to be present in the same workspace, the worst-case-combined safe volume must be determined. Contact your deployed IH and/or the OHS-ISH Cryogen Program (<a href="mailto:cryo@lanl.gov">cryo@lanl.gov</a>) for assistance.

**Note:** If the amounts of cryogens located in a workspace exceed the allowable safe volume,  $V_s$ , the location must be evaluated to determine if adequate levels of ventilation are present. Contact your deployed IH and/or the OHS-ISH Cryogen Program for assistance.

**Important:** The equation in Section 3.3, Revision 3 of <u>P101-5</u>, overestimates the safe volume for inert cryogens with an  $ER_{STP}$  over 720 (i.e.,  $\epsilon \le 14$ ). For argon and neon, you must not use the estimate from P101-5, which overestimates the safe volumes by 10% and 100%, respectively.

The safe volume formula is based on the assumption that no supply or exhaust ventilation is available and that the worst-case scenario is where all of the cryogen is converted directly to gas and uniformly mixes into the space. The safe volume formula is

$$V_s[liters] = \frac{V_w[m^3]}{\epsilon} = \frac{V_w[ft^3]}{\emptyset},$$

where  $V_W$  is the volume of the room that is available for breathable air\* in the workspace [in cubic meters (m³) or cubic feet (ft³)] and  $V_S$  is the safe volume of the liquid cryogen (in liters) that can be brought into the room. Table 5 lists the  $\varepsilon$  and  $\phi$  factors for various inert cryogens and liquefied gases.

\*Note: If you do not perform a detailed estimate, a good rule of thumb is that laboratory space should be reduced by 25% to conservatively account for items in the room. If your workspace contains a pit or confined space, count only the breathable air space volume of the pit or confined space as the volume of your workspace.

Table 5. Safe Inert Cryogen Volume Factors (ε and Φ)

Inert Cryogen or Liquified Gas	ε (m^3/L)	φ (ft^3/L)
Xe	9.91	349.86
Nitrogen	12.79	451.79
Krypton	12.80	451.86
Helium	13.87	489.64
Argon	15.52	548.14
Neon	26.61	939.57

For example, if we assume that the cryogen is liquid nitrogen, this leads to

$$V_{S}[liters] = \frac{V_{W}[m^{3}]}{12.79 \, m^{3}/L} = \frac{V_{W}[ft^{3}]}{451.79 ft^{3}/L}$$
.

Thus, for a 10,000-ft<sup>3</sup> (or 283-m<sup>3</sup>) room, both formulas give a safe volume of 22.1 liters.

If we assume a 25% blockage (i.e., % of volume occupied by equipment; not people) in the room, the volume decreases to 7500 ft<sup>3</sup> (or 212 m<sup>3</sup>), and both formulas give a safe volume of 16.6 liters.

## Safe Volume Questions (answers on page 51)

- 1. You are working in an unventilated room that is 15 feet long, 10 feet wide, and 12 feet high. Your operation calls for cryogenic argon. The safe volume formula allows you to bring how much liquefied argon into the room?
- 2. You are going to perform an experiment using cryogenic nitrogen in an unventilated room that is 4 m long, 4 m wide, and 3.5 m high. Within the room are seven cabinets filled with noncombustible materials. Each cabinet is 2 m tall, 1 m wide, and 1/2 m in depth. The safe volume formula allows you to bring how much liquefied nitrogen into the room?
- 3. You are going to perform an experiment using cryogenic helium in an area within a room that is 7 m long, 1 m wide, and 3 m deep. The area meets the criteria for a confined space and is located in an unventilated room that is 7 m long, 4 m wide, and 3 m high. The safe volume formula allows you to bring how much liquefied helium into the room without a qualified industrial hygienist determining actions needed?
- 4. You are going to perform an experiment that requires 2 L of cryogenic fluorine in an unventilated room that is 5 m long, 4 m wide, and 3.5 m high. Within the room is a pit that is 3.5 m long, 2 m wide, and 3 m deep. The pit meets the criteria for a confined space, but you will not be performing your work within the pit. Also within the room are two cabinets and a refrigerator. each cabinet is 2 m tall, 1 m wide, and 1/2 m deep, and the refrigerator is 2 m tall, 1 m wide, and 1 m deep. Using the safe volume formula, can you bring in the 2 L of cryogenic fluorine?

# **Warning Signs**

Workers who handle cryogenic fluids must be alert for signs or conditions that indicate the buildup of hazardous pressures in cryogenic systems. Such indications include

- an elevated gauge pressure;
- a lack of expected response on a gauge to a valve adjustment;
- unexpected frost formation or its absence;
- the failure of a system to vent normally;

- alarms indicating hazardous concentrations of gas in the work area;
- excessive or unusually frequent vapor release; and
- unexpected noises or the absence of normal venting noise.

# **Emergency Response**

Emergency response procedures must be developed for each cryogenic operation and included prominently in all IWDs. Warning signs and emergency contact information must be posted at the entrance to the area where cryogenic work is being done. Consult P101-5 and contact the OSH-ISH Cryogen Program (cryo@lanl.gov) for assistance.

Examples of cryogen related emergencies include

- a helium Dewar that has an ice plug in the neck;
- a Dewar that drops or falls on its side; or
- the fill tube in your 50-L Dewar that you think has plugged up with ice.

If you experience an accident or incident involving an injurious or life-threatening release of a cryogen,

- leave the immediate area and call 911;
- ensure that others do not enter;
- tell your supervisor as soon as possible;
- report any injuries or illnesses related to the accident to your supervisor and to OSH-OH as soon as possible;
- notify Emergency Management at 667-6211; and
- consult the reporting procedures found in P322-3, Performance Improvement from Abnormal Events.

**Note:** A work area that does not contain air monitors must be evacuated if an inert cryogen spill occurs. When the ventilation system has had sufficient time to refresh the air supply, workers can return to the area. Under emergency conditions where there is an uncontrolled discharge of liquid or gas, as in the case of liquid cylinder failure, entry by personnel other than Emergency Response must be made as a Permit Required Confined Space Entry according to P101-27 Confined Spaces.

# **Answers to Human Performance Improvement Questions (p. 19)**

#### Question 1:

• The researcher and colleague attempted to remove the stuck thermos top.

#### Question 2:

- The thermos was not designed for cryogen transportation.
- The thermos top was screwed on too tightly.
- The thermos may have been stored in too humid of an environment.
- The researcher failed to observe the absence of frost on the top of the thermos.
- The researcher failed to correctly assess the over-pressurized thermos top resistance as an off-normal occurrence and failed to stop/pause work.
- No contingency plan appeared to be in place to address a frozen thermos top.

## **Question 3:**

- Use the proper equipment for the transportation of cryogens.
- Develop guidance that addresses the transportation of cryogens.
- Communicate to persons involved in such activities the hazards, controls, acceptable practices, indicators, and responses to unusual situations applicable to the transportation of cryogens.
- Pause/stop work when confronted with unexpected off-normal situations.
- Determine the appropriate PPE to be used when handling cryogens.

# Answers to Safe Volume Questions (p. 49)

- **Question 1:** 15 ft × 10 ft × 12 ft = 1800 ft<sup>3</sup> in the room. From Table 5 for argon  $\phi$ =548.14 ft<sup>3</sup>/L. Therefore, 1800 ft<sup>3</sup> ÷ 548.14 ft<sup>3</sup>/L = 3.28 L of argon.
- **Question 2:**  $4 \text{ m} \times 4 \text{ m} \times 3.5 \text{ m} = 56 \text{ m}^3$  in the room. From Table 5 for nitrogen,  $\epsilon = 12.79 \text{ m}^3/\text{L}$ . Each cabinet is  $2 \times 1 \times 0.5 = 1 \text{ m}^3$  so for 7 cabinets = 7 m<sup>3</sup>, then 56 m<sup>3</sup> 7 m<sup>3</sup> = 49 m<sup>3</sup>. Therefore, 49 m<sup>3</sup> ÷ 12.79 m<sup>3</sup>/L = 3.83 L of nitrogen.
- Question 3: Because the work will be performed within a confined space, you can consider only the volume of the confined space. From Table 5 for helium, ε=13.87 m³/L. Therefore, 7 m × 1 m × 3 m = 21 m³ ÷ 13.87 m³/L = 1.51 L of carbon dioxide. However, *any* use of a cryogen in a confined space requires evaluation by OSH-ISH.
- **Question 4:** Because fluorine is not an inert cryogen, the safe room volume does not apply. Ask your industrial hygienist!

Module 3: Cryogen	Agencies,	Standards,	and Procedur	es
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Notes....

# **Resources and References**

#### Resources

For help with	contact
a review of hazards, controls, calculations, or system design and engineering for new or existing cryogen systems or storage areas,	Mechanical and Thermal Engineering (AET-1). 667-8091
the determination of hazards or controls, including ventilation, safe room volume determination, or operations involving liquid oxygen, toxic, flammable, explosive, or reactive cryogens,	Occupational Safety and Health (OSH) Cryogen Program or Division Office. 606-0295
cryogen purchase and delivery, or the maintenance and inspection of portable liquid helium storage liquid cylinders,	Operations Support-Packaging and Transportation (OS-PT) (Gas Plant). 667-4406
an ice plug that cannot be removed or any other any emergency involving a cryogen,	Emergency Management. 667-6211

#### References

#### General

- Bartschi, B. Y., D. E. Morse, and T. L. Woolston, "The Spatial Infrared Imaging Telescope III. Johns Hopkins APL Technical Digest, Volume 17, Number 2, 1996;
- Edeskuty, F. J., and W. F. Stewart, 1996, Safety in the Handling of Cryogenic Fluids, Plenum Press, New York;
- The Hendrix Group Reporter, "Hydrogen Embrittlement of High Strength Fasteners," Volume VII, Number 1, June 1997. http://www.hghouston.com;
- Haselden, G. G., 1971, Cryogenic Fundamentals, Academic Press, London;
- Williamson, K. D., and F. J. Edeskuty, 1983, Liquid Cryogens, Vols. I and II, CRC Press, Inc.;
- Zabetakis, M. G., 1987, Safety with Cryogenic Fluids, Plenum Press, New York;
- D. R. Lide, ed., Chemical Rubber Company (CRC), Handbook of Chemistry and Physics, CRC Press, Inc., 78<sup>th</sup> edition, Boca Raton.

#### **Consensus Standards**

# **Compressed Gas Association (CGA)**

- CGA AV-8, "Characteristics and Safe Handling of Cryogenic Liquid and Gaseous Oxygen" (video),
- CGA G-5, "Hydrogen,"
- CGA P-12, "Safe Handling of Cryogenic Liquids,"
- CGA P-13, "Safe Handling of Liquid Carbon Monoxide,"
- CGA, "Handbook of Compressed Gases," and
- CGA SB-9, "Recommended Practice for the Outfitting and Operation of Vehicles Used in the Transportation and Transfilling of Liquid Oxygen to Be Used for Respiration.

# **National Fire Protection Association (NFPA)**

- NFPA 55-2016, "Compressed Gases and Cryogenic Fluids Code."
- NFPA 55-2010, "Compressed Gases and Cryogenic Fluids Code Handbook,"
- NFPA 68-2013, "Standard on Explosion Protection by Deflagration Venting,"
- NFPA 69-2014, "Standard on Explosion Prevention Systems,"
- NFPA 70-2017, "National Electrical Code", Articles 500 through 510, which cover hazardous locations, and
- NFPA 2112, "Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire."

## Code of Federal Regulations (CFR)

- 29 CFR, <u>1910.101</u>, "Compressed Gases (General Requirements),"
- 29 CFR <u>1910.103</u>, "Hydrogen,"
- 29 CFR <u>1910.104</u>, "Oxygen,"
- 29 CFR 1910.1200, Subpart Z, "Hazard Communication,"
- 29 CFR <u>1910.1450</u>, "Occupational Exposure to Hazardous Chemicals in Laboratories," and
- 49 CFR "Transportation, Subtitle B, Subchapter A—<u>Hazardous</u> <u>Materials And Oil Transportation</u>," parts 105 through 180.

# **Department of Energy (DOE)**

• DOE Operating Experience Summary 2012-02, May 11, 2012.

# **Los Alamos National Laboratory (LANL)**

- Procedure P101-5, "Cryogens,"
- Procedure P101-14, "Chemical Management,"
- Procedure P101-27, "Confined Spaces,"
- Procedure P101-34, "Pressure Safety," and
- Procedure <u>P322-3</u>, "Performance Improvement from Abnormal Events," and
- Engineering Standards Manual, Chapter 17, "Pressure Safety."
- LANL Memorandum <u>PADSTE:11-054</u> "Notification of Safety Issue with Dewar Cart and Required Remediation," 25 February 2011.